Low Stress Films of Cyclized Polybutadiene Dielectrics by Vacuum Annealing

M. Salazar
C. W. Wilkins, Jr.
V. W. Ryan
T. T. Wang

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

We report here a vacuum annealing technique for the post-deposition processing of cyclized polybutadiene dielectric (CBR) films. The technique has proven effective in reducing film stress from $3.1 \pm 0.5 \times 10^8$ dynes/cm^2 (tensile) to $1.4 \pm 0.2 \times 10^8$ dynes/cm^2 when the material is thermally cycled between 20 and 280°C. For 10 μm thick films the technique results in a net reduction in Si wafer bow by a factor of two. This reduction in wafer bow is important in the building of multilevel metallization structures where problems with patterning of films and automatic wafer handling equipment are encountered with excessively bowed substrates. A change in the glass transition temperature from ~320 to ~130°C was also observed in the vacuum treated films and mechanical coupling to the substrate was seen to occur at ~175°C instead of 280°C.

Low Stress Films of Cyclized Polybutadiene Dielectrics by Vacuum Annealing

M. Salazar
C. W. Wilkins, Jr.
V. W. Ryan
T. T. Wang

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

INTRODUCTION

Polymer dielectric materials play a significant role as interlayer insulators in multilevel metallization schemes for VLSI. Among these, cyclized polybutadiene rubber (CBR), has shown great potential because of its relatively low dielectric constant (2.6), high thermal stability (~390°C) and ease of processing.[1,2] Unfortunately, like most polymeric materials, films of CBR deposited on Si wafers develop stress after thermal cycling at high temperatures (>200°C).[3] This stress results largely from the mismatch in the thermal expansion of the substrate and polymeric material, but it is also due to the shrinkage which occurs during curing and solvent removal. Excessive stress can lead to film delamination, cracks in the polymer film and substrate bow.

When cured in a nitrogen atmosphere the thermal stress of cyclized polybutadiene films, 10 μm thick, has been found to cause a bow of about 39 μm in a 20 mil thick, 4 inch diameter Si wafer.[4] This value is typical of most organic dielectrics that are used in multilevel metallization processes. Since up to three layers of the dielectric material may be used on a given substrate it is important to find ways of controlling film stress so as to minimize wafer bow. This can either be done by chemically modifying the polymer or by changing post-deposition processing of films.

Chemical modification of polymers which leads to reduced stress has already been achieved with some polyimides but these are not as yet commercially available.[5] Post-deposition processing techniques have been previously used to control stress in inorganic films.[6] However, we do not know of any curing methods that have been developed to reduce stress in organic dielectric films.

We report here on a new vacuum curing technique for the post-deposition processing of the cyclized polybutadiene rubber photoresist JSR, CBR-M901. This method has proven to be effective in reducing film stress and wafer bow. The effect of this curing method on other mechanical properties of this material will also be discussed.

MATERIALS

Low viscosity (26 cps) cyclized polybutadiene rubber photoresist having an average molecular weight ($\bar{M}_w$) of 4.32×10^5 and a polydispersity (ρ) value of 8.20 was obtained from JSR of America, Inc. ACS reagent grade xylene was used to further dilute the material. Si wafers 20 mil thick and 4 inch diameter of <100> crystal orientation were used as the substrates. In order to calculate film stress the wafer bow was measured with the substrates at either room temperature or *in situ*. Chrome-copper coated Si wafers were used to obtain free standing films for measurements of dynamic Young's modulus as a function of temperature. Quartz and sapphire (Al_2O_3) wafers nominally 520 μm thick and 100 mm diameter were used to measure stress as a function of temperature.

EXPERIMENTAL

Prior to deposition of the polymer films the substrates were characterized (i.e. wafer bow measured) by laser leverage techniques.[4] Films 10 μm thick were spray coated using a Zicon Corporation In-Line Conveyor Coating System Model 10,000. The cyclized rubber was further diluted by adding 50 ml of xylene to 100g of material. The spray deposition

parameters needed to obtain the desired 10 μm thickness are listed in Table I. Before pre-baking the films it was necessary to allow the excess solvent to evaporate for 5-10 minutes while maintaining the substrates level in order to assure uniform film thickness. Pre-baking was then done at 80°C in air for one hour using a hot plate. A Mellen Box Oven Model B-122 was used to further anneal the films.

In order to vacuum treat the films the oven was turned on to a setting of 200°C after the chamber had first been evacuated to a gauge pressure reading of 27 inches of mercury. The oven was held at this 200°C setting for 90 minutes while the samples were heated. Due to the thermal lag of the oven this resulted in an effective baking time of only 30-45 minutes at 200°C. After the vacuum curing step was completed the oven chamber was backfilled with nitrogen gas flowing at ~260 ml/min. This setting was maintained for 90 minutes to gives an effective cure of 30-45 minutes at 280°C. The samples were then allowed to cool under a N_2 flow for at least 30 minutes. As a control experiment some films were annealed using the recommended process from the manufacturer. This process consists of first heating the films at 200°C in air for 30 minutes then heating at 280°C in N_2 for 30 minutes.

Free standing films needed to measure dynamic mechanical properties were obtained using 500Å Cr/2500Å Cu films sputtered on Si. The substrates (4 inch wafers) were first spray coated with the CBR and then put through the annealing processes described above. The metal film containing the polymer layer was readily peeled off the Si surface and etched away using a potassium ferricyanide solution. Less than three minutes were required to completely remove the metal to give free standing films of the polymer.

Dynamic mechanical properties were measured using a Rheovibron Model DDV-II made by Toyo Instrument Company, Tokyo, Japan. The dynamic Young's modulus of the sample was measured in N_2 from 20 to 400°C at a rate of about 2°C/min. and a frequency of 110 Hz.

RESULTS AND DISCUSSION

After one thermal cycle the manufacturer's suggested annealing process resulted in a film stress at room temperature of $3.1 \pm 0.5\times10^8$ dynes/cm² (tensile) and a wafer bow of about 39 μm for 10 μm thick films. Using the vacuum annealing process described above the film stress measured $1.4 \pm 0.2\times10^8$ dynes/cm² and the wafer bow was about 19 μm for 10 μm thick films. This represents a net reduction in film stress and wafer bow by a factor of three and two respectively.

Dynamic mechanical data (Figure 1) show that vacuum annealed films have slightly smaller in-phase moduli, E', (2.3×10^{10} dynes/cm²) than those annealed by the manufacturer's recommended curing process (2.9×10^{10} dynes/cm²). However, the glass transition temperature, T_g, as determined from the peak temperature of the out-of-phase modulus (E'') plot is seen to change from ~320°C to ~130°C. Also, films annealed in vacuum at 200°C were found to be very pliable whereas those annealed in air were very brittle. This clearly indicates that a much more compliant material (with a different micro-environment due to more complete solvent removal) results from the vacuum annealing process.

Results of *in situ* stress measurements of CBR films annealed in vacuum are shown in Figure 2. Using the three substrates shown with known thermal expansion coefficient (TEC) it was possible to deduce the relative TEC value for CBR. For the temperature range studied the TEC for CBR was consistently greater than that for sapphire (7.4×10^{-6}/°C) and had a mean value of 13×10^{-6}/°C. However, the stress-temperature curves were found to be non-linear in the temperature regime below 200°C. This non-linear behavior was an unexpected result since most organic and inorganic films normally show a linear relationship between stress and temperature.[7] One possible explanation for this is the low T_g of the vacuum annealed CBR films which become rubbery as the temperature approaches T_g during the heat scan. As the temperature exceeds T_g the combined effect of a larger TEC and faster stress relaxation should bring about a progressively larger decrease of film stress. The *in situ* stress measurements also show that mechanical coupling to the substrate (as indicated by zero stress) occurs at ~175°C for the vacuum annealed films. These films also showed no hysteresis in room temperature stress following repetition of the annealing process. Films of CBR on Si substrates which did not undergo vacuum annealing (dashed curve Figure 2) did show a linear dependence of stress as a function of temperature. However, in this case mechanical coupling to the substrate occurred at ~280°C (extrapolated value) and a hysteresis in room temperature stress (~20% increase) was observed. We were unable to measure stress *in-situ* above 200°C because CBR will oxidize when heated in air above this temperature for prolonged periods of time and the equipment was not available to carry out experiments at high temperatures in an inert atmosphere.

Table II summarizes the differences in mechanical properties of films of CBR annealed using the manufacturer's recommended process vs. those annealed under vacuum. The chemical reactions that occur during the annealing process are not known. However, since the thermal treatment is essentially the same for both types of samples except for the environment to which they were exposed at 200°C, it may be suggested that the films prepared according to the manufacturer's suggested annealing process had undergone extensive crosslinking as a result of their exposure to air at 200°C. Some oxidation may have also occurred and IR studies to investigate this possibility are under current investigation. Future work will be directed at identifying the cause for the reduction in film stress and finding ways to improve the results. Preliminary experiments using other techniques consisting of longer vacuum soak times at 200°C or vacuum annealing at high temperatures have not proven successful in further reducing film stress.

SUMMARY AND CONCLUSION

We have described a vacuum annealing technique for CBR films which effectively results in a reduction of stress by a factor of three. Ostensibly, since the final annealing temperature is the same as that employed in the manufacturer's recommended process, the films can be said to have been cured to the same extent, yet they show different mechanical properties. A definite explanation for these differences is yet to be determined. However, this change in the mechanical properties is beneficial in that the net result is a reduction in wafer bow by a factor of two. This is very important in the manufacture of devices where problems with patterning of films and automatic wafer handling equipment are encountered with excessively bowed substrates.

ACKNOWLEDGEMENTS

Helpful discussions with Alan M. Lyons are gratefully appreciated.

REFERENCES

[1] T. Tsunoda, K. Harada, M. Ichikawa, Society of Plastics Engineers, Regional Technical Conference, "Photopolymers Principles — Processes and Materials," Ellenville, NY, p. 84, 1976.

[2] H. Ito, Y. Mizushima and A. Takepa, Jap. J. of Appl. Phys. 19(8), p. 2460 (1980).

[3] T. Igarashi, S. Kondo and M. Kurokawa, Polym., 20, p. 301 (1979).

[4] V. W. Ryan, A. W. Lin, unpublished results. May 29, 1985.

[5] Hitachi News Release No. 84-129, Oct. 9, 1984.

[6] D. S. Williams, J. Appl. Phys. 57 (6), p. 2340 (1985).

[7] T. F. Retajczyk, Jr., A. K. Sinha, Appl. Phys. Lett. 36, 161 (1980).

TABLE I

MATERIAL PRESSURE (IN. OF WATER)	50
ATOMIZATION PRESSURE (IN. OF WATER)	15
TRAVERSE SPEED (IN/S)	16
CONVEYOR SPEED (IN. PER SPRAY STROKE)	1/2
SPRAY GUN HEIGHT (IN.)	6.5
NOZZLE DIAMETER (mm)	0.5
SPREADER TYPE	RB5

TABLE I. Spray deposition parameters needed to obtain cured CBR-M901 films 10 μm thick.

TABLE II

MECHANICAL PROPERTY	NO VACUUM	VACUUM ANNEALED
STRESS (dynes/cm^2)	$3.1 \pm 0.5 \times 10^8$	$1.4 \pm 0.2 \times 10^8$
WAFER BOW (10 μm THICK FILM)	≈39 μm	≈19 μm
DYNAMIC VISCOELASTICITY (110 Hz) IN-PHASE MODULI (dynes/cm^2)	2.9×10^{10}	2.3×10^{10}
T_g	≈320°C	≈130°C
TOUGHNESS (FREE FILM)	BRITTLE CRACKS EASILY	PLIABLE
MODULUS vs TEMP (25-200°C)	≈LINEAR	NON-LINEAR
STRESS vs TEMP (25-200°C)	≈LINEAR	NON-LINEAR

TABLE II. Comparative mechanical properties of CBR films annealed per manufacturer's suggested process (no vacuum) vs. those annealed in vacuum.

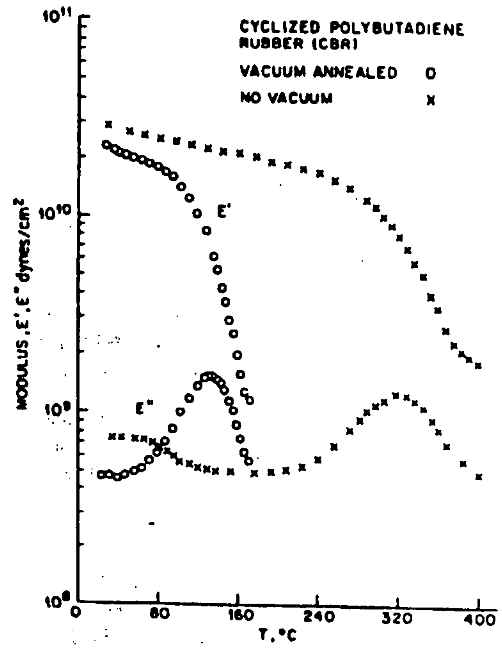

Figure 1

Figure 1. Dynamic mechanical properties of CBR-M901 films. Vacuum annealed film (o), film annealed per manufacturer's suggested process (x).

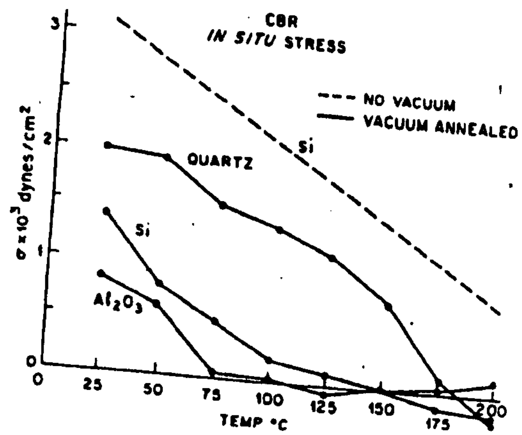

Figure 2

Figure 2. Stress-temperature *in-situ* measurements of vacuum annealed CBR-M901 films (solid lines) and film cured using the manufacturer's suggested annealing process (dashed line).

PROCESSING CONCERNS FOR MULTI-LEVEL THIN FILM METALLIZATION

C.Narayan, J.Lewis, S.Purushothaman, E.Castellani, D.Shih and J.Fugardi.[▲]
IBM Research, Yorktown Heights, NY 10598
[▲]IBM-GTD, Hopewell Jn., NY 12355

ABSTRACT

Evaporation of multi-layer metallic thin film structures, bearing reactive metals like Ti, requires good control over the metallization process. During sequential deposition, the delay between the deposition of Ti and the next layer (X) and the pressure in the evaporation chamber during metallization, determine the impurity contents at the Ti/X interface which in turn influences the electrical and mechanical properties of the structure. If the starting pressures are less than 3×10^{-4} Pa and the delay between the deposition of Ti and X is less than 23 minutes the electrical resistance of the structure is low and is process independent. The mechanical strength of the structure is, however, more sensitive to contamination at the Ti/X interface. The use of multiple electron gun systems to eliminate delay during deposition and the practice of pre-evaporating Ti, to clean the chamber prior to evaporating the thin film structure, will ensure electrically and mechanically sound structures.

INTRODUCTION

Multi-layer metallic structures are becoming increasingly important in the electronics industry. To produce good multi-layer thin films, metallization techniques like evaporation have to be well understood and controlled. During the fabrication of thin film structures containing reactive metals like Cr, Zr or Ti, improper evaporation practice can lead to the contamination/oxidation of the reactive surfaces, which in turn will degrade the performance of the structure. Kemmerer and Mills[1] have shown that Ti/Cu interfaces delaminate if processing chamber pressures are not carefully controlled. If contamination at the interface is not adequate to cause delamination of the